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ORIGINAL PAPER

Mechanical and electrical stability of parylene-based platinum-black coated wire microelectrode for implantable applications

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Abstract In this paper, a parylene-based platinum-black coated wire microelectrode with multi-electrode sites for neuromuscular stimulation was fabricated. The electrodes with tunable electrode site position, quantity, and width will achieve multi-stimulation during functional electrical stimulation. The platinum-black coating was electroplated on electrode sites by applying a current pulse train in chloroplatinic acid solution (H_2PtCl_6) under ultrasonic bath, which contributed to achieve excellent mechanical and electrical stability of the microelectrode. After electroplating, the 90 % of impedance reduction and 13 times of cathodic charge storage capacity increase were achieved. Finally, the mechanical and electrochemical stability test, the passive soaking test, and the bending test were performed. The results showed that the platinum-black coated wire microelectrode had good stability after 5 min of ultrasonic vibration and 122 h of current pulses stimulation. After soaking in 0.9 % saline solution at 87 °C for 8 months, the average impedance at 1 kHz just increased by 1.6 kΩ. The bending test (with maximum bending angle of 90°) also showed that there was a little change in the electrochemical characteristics of the electrode. This parylene-based platinum-black coated wire microelectrode will be promising for facial prosthesis applications.

Keywords Parylene · Platinum-black · Microelectrode · Facial prosthesis · Implantable

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1 Introduction

Facial paralysis often causes the loss of tone, dysfunction of the eye closure, and facial expressions due to facial nerve injury [17, 18]. The most serious consequence for the patients with facial paralysis is blindness because of the functional deficits in the ability of closing the eyelids. The reasons for facial nerve injury usually include palsy, trauma, infection, and inflammation. The current methods such as nerve grafts [6], FES [15], and other auxiliary treatments [1, 3, 9, 10] are usually deployed for facial paralysis treatments. The disadvantages of nerve grafts include the insufficient available nerves in surgery, the poor biocompatibilities and degenerative capacities of the artificial nerves, and the little chance for patients with severe facial nerve damage. The auxiliary treatments are composed of the implantation of gold weights in the eyelid, the implantation of mechanical springs, the use of artificial tears, and so on, which are also limited by their inconvenient applications and imperfect effects [4]. FES is the application of electrical current to excitable tissue to supplement or replace function that is lost in neurologically

impaired individuals. The stimulation of denervated muscle will lead to muscle contraction. In order to rehabilitate eye blink of the patients with facial nerve paralysis, the stimulation of orbicularis oculi muscle (OOM) which controls the movement of eyelid will be an effective method. For charge delivery during FES, the stimulation microelectrodes with low impedance, high selectivity, and CSC (charge storage capacity) are desired to reduce power consumption and improve stimulation effects. Due to the contradiction between low impedance and high selectivity, the methods such as micropatterning [2], electroplating [7], surface roughening [14], and chemical modification [5] can solve this problem due to the increase in the effective area of microelectrodes. Furthermore, to achieve small wound, quick recovery, improved cosmesis, and stimulation effects, the wire microelectrodes with multi-electrode sites will be a good choice because of its good flexibility, small area, and multi-stimulation function [16]. Figure 1 shows the schematic diagram of the wire microelectrode with multi-electrode sites. Nano structures integrated on electrode sites can significantly increase the effective area of microelectrode [20]. For further improving the electrochemical characteristics of wire microelectrodes, platinum-black coatings integrated on electrode sites with good biocompatibility and simple fabrication process [12, 16] can be applied. The conventional constant potential electroplating method would result in porous and thick coatings, which can obviously reduce the impedance and increase cathodic charge storage capacity (CSCc). However, the coatings could be easily damaged due to the poor adhesion, which would result in unstable electrochemical characteristics of the electrodes. Compared with constant potential electroplating, ultrasonic electroplating and current pulse electroplating can refine grain during the electroplating process [11, 19], which contributes to good adhesion between coatings and substrates. For long-term implantation applications, such as spinal cord stimulation system, cardiac pacing system, artificial prostheses, and so on, the stability of stimulation electrodes is a crucial factor; the electrodes with good stability will ensure the reliability and stability of the implantable system after long-term implantation. How to evaluate the stability of the electrodes is necessary.

In this paper, the sacrificial process was deployed to fabricate the wire microelectrode with multi-electrode sites, and the current pulse train under ultrasonic bath was applied to fabricate the platinum-black coatings for further improving the characteristics of microelectrode. In addition, the mechanical and electrical stability test, the passive soaking test, and the bending test were performed to evaluate the stability of the microelectrode for long-term implantation.

2 Experiments

2.1 Electrode fabrication

Platinum wire (diameter = 100 μm, 99.95 %, BYB) was prepared and cleaned in an acetone ultrasonic bath, and polydimethylsiloxane (PDMS) thin films (thickness = 100 μm) were spin coated on wafer to serve as sacrificial layers. Then the sliced PDMS thin films (2 mm × 2 mm) were pierced through by platinum wire at the position of electrode sites. After that, a layer of parylene C thin film (thickness = 5 μm) was deposited on platinum wire by a parylene deposition system (PDS 2010, SCS, USA) to serve as insulation layer. Finally, the PDMS thin films were removed to expose the electrodes sites.

2.2 Electroplating

In order to improve electrode characteristics, platinum-black coatings were electrodeposited on electrode sites to reduce impedance and increase CSC. The platinum-black coatings were electroplated on electrode sites under repetitive current pulse (duty ratio of 5:500 ms, peak current density of 4.5 A/cm^2, and cycles of 480). This pulse was generated in chloroplatinic acid solution (3 % chloroplatinic acid and 0.01 % lead acetate in deionized water) placed in ultrasonic bath (50 W, 40 kHz) by a electrochemical workstation (CHI660B, Chenhua, China).

2.3 Electrochemical characterization

During the electrochemical measurement, a saturated calomel electrode (SCE) and a platinum electrode were used as reference electrode and counter electrode, respectively. Figure 2 shows the schematic diagram of the electrochemical

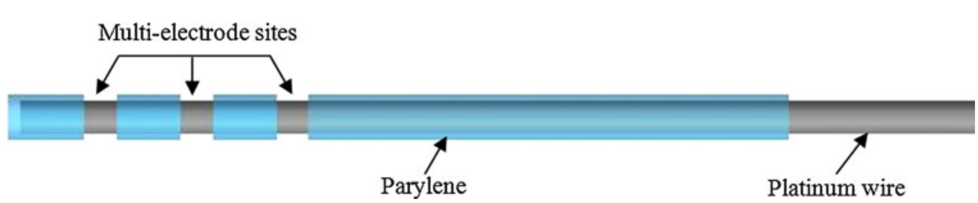

Fig. 1 The schematic diagram of the wire microelectrode with multi-electrode sites

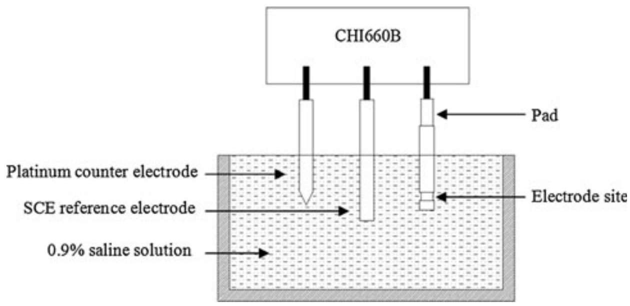

Fig. 2 The schematic diagram of the electrochemical characterization measurement system

Fig. 3 The passive soaking test

characterization measurement system. Electrochemical impedance spectroscopy (EIS) measurements were made in 0.9 % saline solution by 10 mV AC sinusoid signal and at a frequency range from 100 kHz to 0.1 Hz at the open circuit potential (vs. SCE). CSCc were examined by cyclic voltammetry (CV) scanning in 0.9 % saline solution with a CHI660B between potentials of 0.8 and −0.6 V (vs. SCE) at a scan rate of 50 mV/s.

2.4 Mechanical and electrochemical stability test

The mechanical stability of the platinum-black microelectrodes was evaluated by observing the decline of CSCc following an ultrasonic bath (50 W, 40 kHz) at room temperature for 5 min [13]. Then, the electrodes were rinsed with deionized water, and stabilized in 0.9 % saline solution for 30 min. Due to the average blink frequency of 10,000 times per day for one person, the blink times of one person in 60 years can be calculated as 2.19×10^8. Assuming that one stimulation pulse can make the eye blink once, the amount of 2.19×10^8 stimulation current pulses should be applied during the test. The electrochemical stability of the platinum-black microelectrodes was evaluated by observing the decline of CSCc following 2.19×10^8 anodic-first current pulses (duration of biphase of 1 ms, frequency of 500 Hz, and peak current of 0.1 mA) in 0.9 % saline solution at room temperature.

2.5 Passive soaking test

In order to evaluate the life-time of the platinum-black coated wire microelectrode, the passive soaking test was performed. In this test, six microelectrodes with platinum-black coatings were put into six glass tubes filled with 0.9 % saline solution and placed into convection oven at 87 °C for 8 months. For the prevention of water evaporation, the weekly refilling of water was necessary. The EIS and CV were measured by CHI660B periodically. Figure 3 shows the passive soaking test. The active soaking test at 87 °C would be expected to cause electrode failure faster, and this should be planned in future work.

2.6 Bending test

The flexible wire microelectrodes will bend when the muscle contracts, which would affect the coatings on electrode sites. In order to evaluate the bending stability of the microelectrodes, four platinum-black coated wire microelectrodes were bent with 30°, 45°, 60°, and 90°, respectively. Then the impedance (at 1 kHz) and CSCc of the sample microelectrode were measured after 0, 1, 10, 20, and 30 times of bending process, respectively. Figure 4 shows the schematic diagram of the bending angle.

3 Results and discussion

3.1 Morphology

Figure 5a shows the platinum-black coatings fabricated by constant potential electroplating method. As can be seen from the figure, the platinum-black coatings with large particles on electrode site are porous and thick, which will reduce the charge transfer rate during FES and affect the stimulation effects. These large particles result in the poor adhesion between substrates and coatings. Thus, the coatings cannot be effective after long-term implantation. Figure 5b shows the platinum-black coatings fabricated by

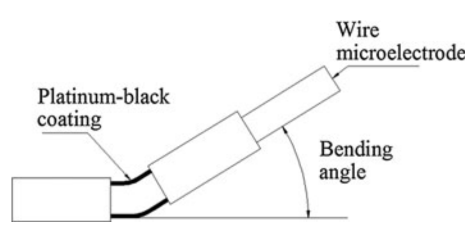

Fig. 4 The schematic diagram of the bending angle

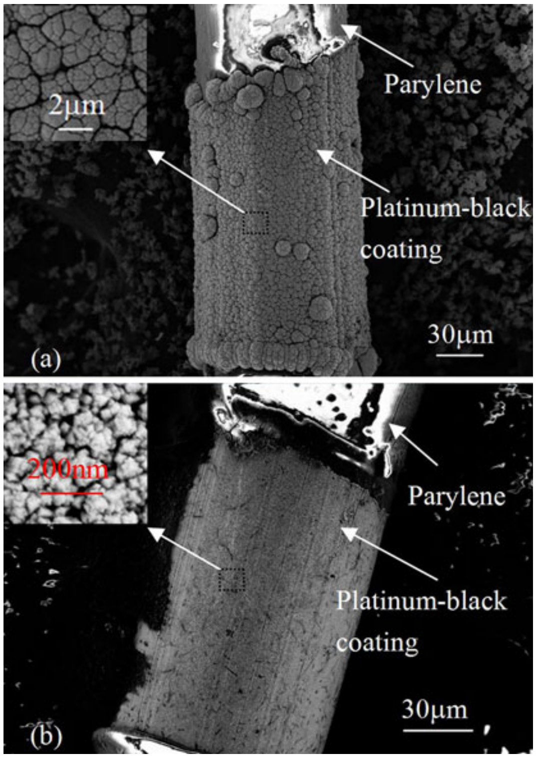

Fig. 5 Platinum-black coated wire microelectrode. **a** Platinum-black coatings fabricated by constant potential electroplating. **b** Platinum-black coatings fabricated by current pulse train electroplating under ultrasonic bath

current pulse train electroplating under ultrasonic bath. The thinner coatings with small particles can be successfully electroplated on electrode site. Due to high peak current and ultrasonic power during electroplating process, the smaller platinum nanoparticles are achieved which will greatly enhance the adhesion force between substrates and coatings. The concentration of the electroplating solution in the ultrasonic bath will be more uniform, which is helpful during electroplating process.

3.2 Electrochemical characteristics

In order to study the relationship between the increase of effective surface area and the change of electrical characterization, a widely used circuit model was adopted as shown in Fig. 6. Based on this model, the impedance and the phase angle of the electrode–electrolyte interface can be given by the following Eqs. (1) and (2), respectively:

$$Z = \frac{R_t + R_s + R_s\omega^2 C_d^2 R_t^2 - j\omega C_d R_t^2}{1 + \omega^2 C_d^2 R_t^2} \quad (1)$$

$$\theta = -tg^{-1}\frac{\omega C_d R_t^2}{R_t + R_s + R_s\omega^2 C_d^2 R_t^2} \quad (2)$$

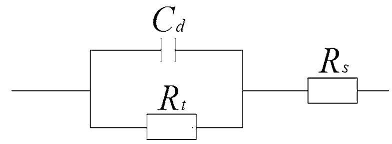

Fig. 6 The equivalent circuit of electrode-tissue interface (Cd, Rt, and Rs represent double layer capacitance, charge transfer resistance, and solution resistance, respectively)

where Z is the impedance, θ is the phase angle, R_t is the charge transfer resistance, R_s is the solution resistance, C_d is the double layer capacitance, and ω is the angular frequency. At higher frequency, R_t will be shorted by C_d which makes the impedance tend to be R_s. At lower frequency, C_d is open circuit which makes the impedance tend to the sum of R_t and R_s. The phase angle will vary from 0° to 90° with the change of the testing frequency.

In the experiment, the impedance of platinum-black microelectrodes at 1 kHz was reduced to 1.58 kΩ after platinum-black deposition, which is 90 % smaller than that of the platinum microelectrode (15.12 kΩ). The significant reduction of impedance resulted from an increase in C_d of the platinum-black coatings; the value of C_d of these microelectrodes increased from 0.024 to 0.38 μF as well, which was consistent with the previous description. The CSCc was calculated from the time integral of the cathodic current in a 50-mV/s sweep-rate cyclic voltammogram over a potential range from 0.8 to −0.6 V. A significant increase of the area of the CV curve showed the great increase of CSCc. After electroplating, the CSCc of platinum-coated microelectrodes (1.697×10^{-5} C) was 13 times as much as the CSCc of platinum microelectrodes (1.315×10^{-6} C) which is desired for neuromuscular stimulation.

3.3 Mechanical and electrochemical stability

Figure 7 shows the CV of platinum-black coated microelectrodes before and after 5 min of ultrasonic vibration (50 W, 40 kHz) for mechanical stability evaluation. Compared with constant potential electroplating process with the CSCc loss of 66 %, the adhesion force between substrates and coatings was enhanced by grain refinement and only 21 % CSCc loss was observed after mechanical stability test. The result showed the good mechanical stability of the platinum-black coated wire microelectrode.

Figure 8 shows the CV of platinum-black coated microelectrodes before and after 2.19×10^8 anodic-first current pulses stimulation for electrochemical stability evaluation. Compared with the CSCc before stimulation (2.88×10^{-5} C), little change of CSCc has occurred after stimulation (2.80×10^{-5} C). The result demonstrated the

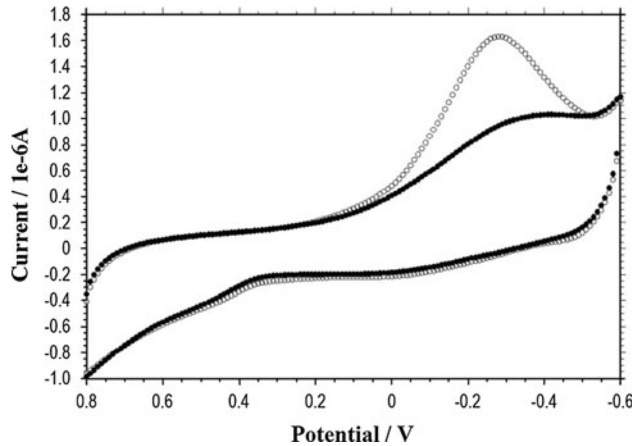

Fig. 7 CV of platinum-black coated microelectrodes before (*open circle*) and after (*filled circle*) 5 min of ultrasonic vibration for mechanical stability evaluation

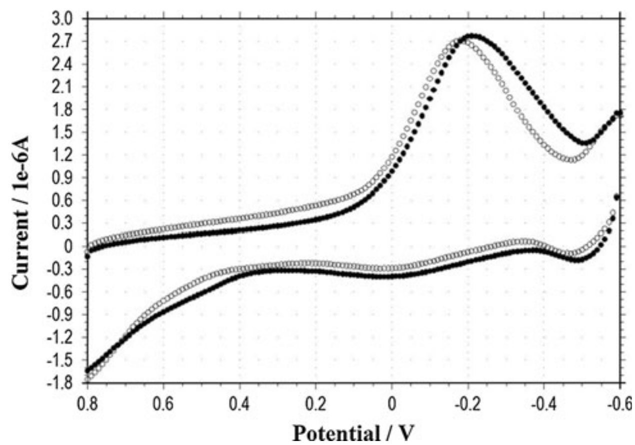

Fig. 8 CV of platinum-black coated microelectrodes before (*open circle*) and after (*filled circle*) 2.19×10^8 anodic-first current pulses stimulation for electrochemical stability evaluation

excellent electrochemical stability of the platinum-black coated wire microelectrode.

3.4 Passive soaking characteristics

Based on the empirical relationship that an environmental temperature increase of 10 °C doubles the effective time [8], the acceleration factor can be calculated by following formula:

$$\mathrm{AF} = 2^{\frac{T-T_0}{10}} \tag{3}$$

where AF is the acceleration factor, T is the practical temperature in the experiment, and T_0 is the equivalent temperature. In the experiment, T_0 (body temperature) and T were set as 37 and 87 °C, respectively. Based on Eq. (3), the acceleration factor is 32. Thus, the 8 months of soaking at 87 °C can be equivalent to 21.3 years of soaking at 37 °C.

During the passive soaking test, the impedance and the CSCc of six sample wire microelectrodes were measured periodically. Table 1 shows the impedance and CSCc of six sample wire microelectrodes before electroplating, after electroplating, and after 8 months of soaking, respectively. As can be seen from the table, the impedance increase of these microelectrodes at 1 kHz varied from 0.66 to 2.89 kΩ after 8 months of soaking; the average increase of impedance (1.6 kΩ, 1 kHz) also can be obtained from the table. Figure 9 shows the relationship between the impedance of six sample wire microelectrodes and time. The increased trend of the impedance during the test can be observed. The CSCc of these microelectrodes decreased from 57 to 70 % after 8 months of soaking; the average decrease of CSCc (63.5 %) also can be obtained from the table. Figure 10 shows the decreased trend of the CSCc over time during the test.

Although the changing trend of the impedance and the CSCc of six microelectrodes is similar, there were fluctuations between different microelectrodes. The impedance was determined by C_d, R_t, and R_s at the same test frequency. During the passive soaking test, the thickness of the coatings decreases over time, which would lead to the decrease of R_t and C_d; the long-term soaking also could increase the electrode site area due to liquid penetration, which results in decreasing the R_s. So the impedance curves fluctuated due to the variations of R_t, C_d, and R_s. The CSCc curves fluctuated due to the variations of the coating thickness and electrode site area as well. As can be seen from Figs. 9 and 10, there were relatively significant changes in both impedance and CSC during the first month of soaking; their curves gradually became flat after the first month of soaking. The obtained curves demonstrated good stability of the platinum-black coated microelectrode after the first month of soaking which might also indicate the possibility of stability after implantation; in the future work, the implantation experiment of the platinum-black coated microelectrode will be undertaken.

3.5 Bending test

Figures 11 and 12 show the impedance and CSCc of four sample platinum-black coated wire microelectrodes after bending with different angles, respectively. After 30 times bending, the increase rates of the impedance at 1 kHz were 4.5, 15.8, 5.6, and 8.6 % for bending angles of 30°, 45°, 60°, and 90°, respectively. Meanwhile, the corresponding decrease rates of the CSCc were 13, 18.6, 15.4, and 16.2 %, respectively. For No. 2 electrode, the greater impedance increase and CSCc decrease due to its larger electrode site area which could lead to greater loss of the platinum-black nano particles after bending. The flat curves of both impedance and CSCc showed the little changes of

Table 1 The impedance and CSCc of six sample wire microelectrodes before electroplating, after electroplating, and after 8 months of soaking

Electrode number	Impedance(kΩ,1 kHz)				CSCc (μC)			CSCc decrease (%)
	Before	After	8 month	Increase	Before	After	8 month	
No. 1	25.12	1.51	3.72	2.21	2.20	15.1	5.97	60
No. 2	21.88	1.29	1.95	0.66	0.83	39.4	11.9	70
No. 3	22.91	1.64	2.63	0.99	0.82	11.9	5.13	57
No. 4	15.85	1.26	1.96	0.70	1.64	33.1	14.3	57
No. 5	23.44	1.58	4.47	2.89	0.87	21	6.81	68
No. 6	20.89	1.53	3.63	2.10	3.44	18.3	5.74	69

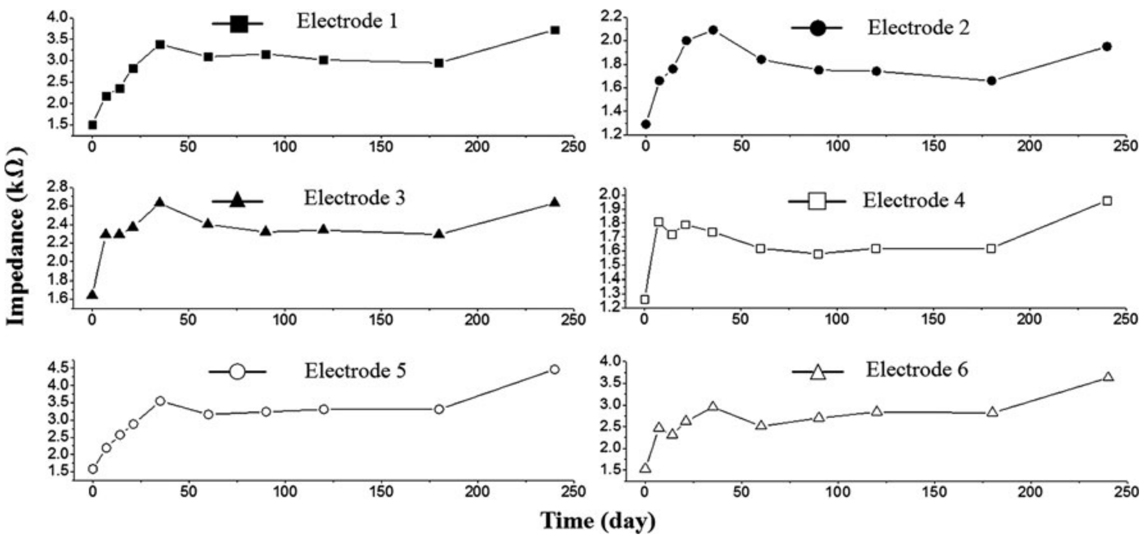

Fig. 9 The impedance of six sample wire microelectrodes varies over time

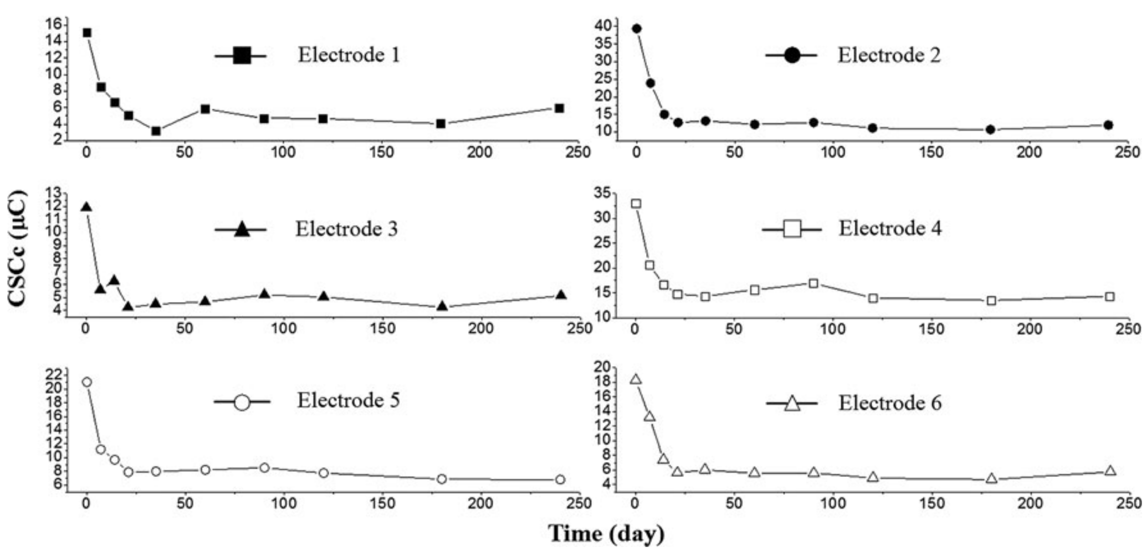

Fig. 10 The CSCc of six sample wire microelectrodes varies over time

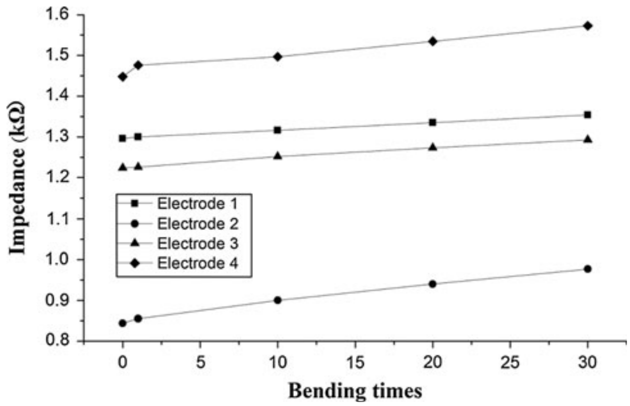

Fig. 11 The impedance of four sample platinum-black coated wire microelectrodes after bending in different angles. *Electrode No. 1*, *electrode No. 2*, *electrode No. 3*, and *electrode No. 4* were bent in 30°, 45°, 60°, and 90°, respectively

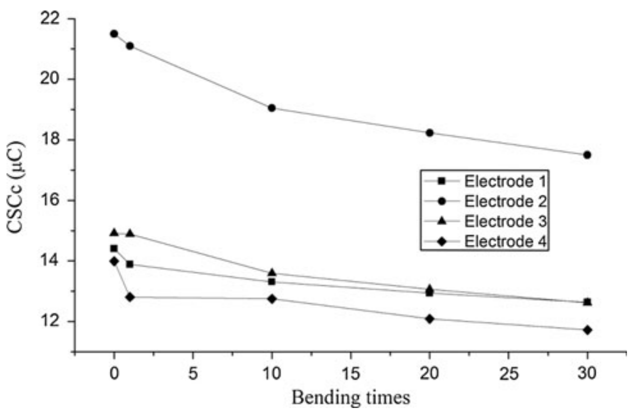

Fig. 12 The CSCc of four sample platinum-black coated wire microelectrodes after bending in different angles. *Electrode No. 1*, *electrode No. 2*, *electrode No. 3*, and *electrode No. 4* were bent in 30°, 45°, 60°, and 90°, respectively

the impedance and CSCc after 30 times bending, which demonstrated good mechanical stability of the platinum-black coatings.

4 Conclusion

In this paper, the platinum wire microelectrodes with multi-electrode sites were successfully fabricated by sacrificial process; the electrodes with tunable electrode site position, quantity, and width would be helpful to specific stimulation cases in FES. The platinum-black coatings were electroplated on electrode sites by applying a current pulse train in chloroplatinic acid solution in ultrasonic bath, which could reduce electrode–tissue interface impedance and obtain good mechanical stability. The results of the EIS and CV also indicated a significant impedance reduction and CSCc increase; the stability test showed good mechanical stability and electrochemical stability of the platinum-black coatings. Moreover, the equivalent to 21.3 years of passive soaking test showed little changes in impedance and CSCc after a month of soaking. Finally, the little change of the impedance and CSCc after bending also demonstrated good bending stability. All of these are desirable for neuromuscular stimulation. This platinum-black coated wire microelectrode will be promising for implantable prosthesis applications.

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